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ELEMENTAL COMPOSITION OF SUSPENDED PARTICULATES AS FUNCTIONS OF SPACE AND TIME IN CLEVELAND, OHIO

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Summary

The information in this paper should be of interest to those people concerned with the temporal and spatial distributions of elements in the ambient TSP and with methods for determining their interrelationships.

In this report we demonstrate an approach to the analysis of a very large elemental concentration data set. The particular data considered was generated by instrumental neutron activation and emission spectroscopy analyses of over 750 24-hour ambient air particulate samples collected at 16 sites in Cleveland, Ohio, during the 15 months from August 1971 thru October 1972. Examples are presented that show the use of multiple approaches to interpreting the data, including pairwise correlation statistics, selective data plotting and cluster analysis.

Despite the large variability of meteorological conditions during the sampling period, as well as the considerable accuracy and precision errors, it was still possible to extract useful information. Br and Pb, taken as a pair, have relatively low variability, are significantly and similarly enriched when normalized to Si as compared with typical earth crustal abundances, and can be used to help distinguish between monitoring sites. The 5 rare earths La, Sm, Eu, Dy and Th generally exhibit the same spatial distribution pattern as Al, Si, Ti, Se and V. As a group they are not highly variable, nor do they show any enrichment relative earth crustal abundance when normalized to Si. This is quite reasonable for Cleveland and could be the super position of a natural background and the emissions from numerous coal burning sources. Fe, Cr and Co jointly exhibit a slightly more variable distribution pattern and with a possible indication of some enrichment. This is to be expected in a city with major iron and steel works. Cu, Mg and Sb are each significantly enriched and each has its own distinctive distribution pattern. The data can also be classified on the basis of the prevailing wind at the time of sample collection and plotted as pollution roses to achieve a very effective visualization of a large body of data. An example is shown for Sc.

In the course of this study it became apparent that standard 24-hour hi-vol sampling does not produce data with sufficient resolution to answer many questions of interest, particularly those regarding source identification. It is our belief that with the proper sampling techniques and extensions of the data analysis methods described above, trace element analysis can provide accurate and economical answers to many of the yet unanswered questions concerning the sources, transport and disposition of particulate aerosols.

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Introduction

In recent years a number of studies in a variety of locations[1-8] have been made of the elemental composition of suspended particulate aerosols (TSP). In general, the goals of these studies, in order of complexity, have been (1) to provide a characterization of the TSP, (2) to use the elemental distributional information to separate out the "natural" background component of the TSP from the component arising from human activity, and (3) to identify the specific human activities which are significant pollution sources.

This report is addressed to items (2) and (3) above as applied to a data set based on over 750 samples taken at 18 sites in Cleveland, Ohio over a period of 15 months. Use was made of standard statistical techniques, such as pairwise correlation analysis, in addition to cluster analysis algorithms, and pollution-rose plots. Examples are given of the application of these techniques to the sorting of elements into related groupings as well as to the effort to distinguish geographic sites by their specific elemental characteristics. These tools are augmented by considering enrichment factors in the ambient aerosol relative to earth crustal distributions typifying this region for these same elements. The large size of our data base enables us to consider the significance of the wind in transport processes and the use of wind specific elemental data to understand pollution transport. Where applicable, we discuss our results in relation to studies in other locations.

Experimental Methods

Sample Collection

In early 1971, a comprehensive study of the suspended particulate matter (TSP) in Cleveland, Ohio was initiated by NASA Lewis Research Center (LeRC) in cooperation with the Division of Air Pollution Control (DAPC) of Cleveland. The purpose of that study was to identify, quantify and characterize the TSP with resolution sufficient to produce statistically meaningful results. The full scope of this program as well as a summary of much of the quantitative results are presented elsewhere[9,10]. As part of that program, DAPC operated a 16 site high-volume sampling network (see Figure 1) over a 15 month period starting in August 1971, for the specific purpose of obtaining TSP samples that could then be analyzed by LeRC for elemental content. It was this specific aspect of the total monitoring effort that generated the data for the present report. Whatman-41 filters were used as the filtering medium because of their compatibility with the elemental analysis techniques employed. A separate report has already been issued which covers the specifics of this network operation and includes the handling and calibration procedures for the Whatman-41 filters[11].

Data Selection

The hi-vol samplers operated from midnight to midnight every 3rd day.

For a number of reasons (e.g., power failure) not all sites provided TSP samples suitable for analysis on every sampling day. The cost of analysis placed a further constraint on the total number of analyses. In order to have maximum spatial resolution it was decided to select particular days and then to analyse all the valid samples for that day. Attention was given to the number of filters available - with preference given to those days with the most nearly complete sets of TSP samples. Some days with lesser numbers of TSP samples were also selected to assure that the final data set would have data representative of the meteorological parameters for Cleveland. The actual number of filters analysed was somewhat over 750. The data base just described is considerably larger than those of any other study known to the authors.

On 2 days in our study period analyses were performed on the TSP samples from all 16 sites and on 4 additional days from 15 sites. Since for these 6 days it was possible to apply our analytical tools in a manner that emphasizes the interrelationships of the elemental distributions and the specific monitoring sites, these 6 days, or occasionally one of them, receive emphasis in this report. These 6 days are tabulated in Table I along with a brief summary of their meteorology for the 6 days as recorded by N.O.A.A. at their weather station at Cleveland Hopkins International Airport[12]. Days 1, 2, and 6 are typical of this region. The weather on days 3, 4, and 5 was less typical in that it was part of a weather system which was almost unchanged for 8 days. Also shown at the bottom of Table I are the identities of the missing samples.

Accuracy and Precision

Except for 5 elements, all analyses were made by Instrumental Neutron Activation Analysis. Most of this work was done at the LeRC Plum Brook reactor facility. Sheibley[13] estimated typical accuracies of ±25% and precisions of ±12%. The two other laboratories whose results are included in this study used the same general techniques and presumably have comparable accuracy[10]. Be, Si, Cd, Bi and Pb were determined by a single laboratory using emission spectroscopy. Accuracy was estimated[10] at ±25%, while the precision is of the order of ±10%. In many instances these analytical techniques only yield upper limits for elemental concentrations. This report only considers those 34 elements for which quantitative results were obtained on at least 85% of the analyses, namely: Na, Al, Si, Cl, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Se, Br, Rb, Ag, Cd, Sn, Sb, Cs, La, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Hg, Pb, Bi, Th. For these elements, measurements that were below detection limit were replaced by a random value from 0.6 to 1.1 times the minimum detected value for that element.

Two other sources of error require comment. The accuracy of hi-vol sampling is unknown. The precision of our hi-vol sampling for TSP[11] was of the order of ±15% whether we used Whatman-41 or glass fiber as the filtering medium. Because the elemental analyses are performed on only small segments of the sample a further error of ±5% is present due to the variability the distribution of particulate matter across the active filtering surface. The cumulative effect of all these errors is to attach an uncertainty at the 0.95 confidence level of about ±30% to each value. This is apart from any

statistical uncertainty that always arises when using the limited sample set as estimators of the actual values for a much larger population.

Results and Discussion

Pairwise Analysis

Table II gives estimated pairwise correlation coefficients for 5 pairs of elements. Co-Sc, Sc-Th and Zn-Sb are tabulated because they had the highest values in the study by Dams, et al.[1] in their study of Gary. Cs-Rb is included because it had the highest value in Cleveland on March 1, 1972. The final pair, Br-Pb, has received attention recently as an indicator of the impact of the automobile on air quality[2,3]. It should be emphasized that there are differences in the data bases used for estimating the correlations. The first 2 columns are correlations across all the monitoring sites in Cleveland for the days shown (see Table I). The Gary values[1] are for 25 sites on one day while the San Francisco values[4] are for 9 sites on one day. The Ivory Coast study was performed at 20 sites over 2 5-day sampling periods while the Paris study was conducted over 8 separate days at 5 sites. The final 3 columns are for 3 specific sites in Cleveland. Site 1 is just east of the industrial valley, site 12 is in a residential neighborhood with some industry to the northwest and site 20 is at the shore of Lake Erie with some light industry to the south. These correlation values are for a single site over an entire year with about 30 to 40 values entering each calculation. Table II is included because this seems to be the easiest and most direct method of reducing data from different sources to a common format which then allows comparisons to be made. However, in light of the relatively small size of the data sets coupled with the rather large percent errors in each measurement, we wish to remind the readers of the necessary caution regarding the interpretation of such information as has been noted by Bogen[7].

Viewing pairwise plots of the data can often be instructive. Figure 2a shows such a sample plot of lead vs. bromine taken from site 17 for the entire study period. With the exception of 2 points, the linearity of the data is rather good considering the uncertainty in each measurement. The mean ratio is 0.31 which is well within the range of values reported for Br/Pb arising from automotive emissions. Another way of looking at these data is to plot all the values for the 6 days listed in Table I while retaining the information concerning the location at which the data were generated. This is shown in Figure 2b. The numbers on the plot are the sites corresponding to Figure 1. It becomes fairly apparent that site 13 which is the only site at ground level and is to the south (generally upwind) from the nearest source of traffic has consistently low values. On the other hand, site 17 which is on the roof of a fire station (could the Pb and Br be coming from inside the building?) and at the intersection of 2 heavily travelled commercial streets has consistently high values.

Multi-parameter (Cluster) Analysis

A number of efforts have been made to extract groupings (clusters) from trace element data sets in order to differentiate among various classes of

sources (e.g., earth's crust, industrial activity) or to further differentiate between specific sources (e.g., auto emissions, powerplants).

Cluster Analysis. One approach is to view this as a problem in pattern recognition amenable to the techniques of cluster analysis. This conceptual approach has been tried by at least 3 other authors. The logic used by Belot et al.[6] is very similar to the logic of our analyses. However, the work by the other two investigators[1,4] was performed in the early stages of the development of clustering theory. Unfortunately they chose an algorithm developed for the social sciences and which is not applicable to the problem at hand. Thus we will restrict our comments in this section to a comparison with Belot's results for Paris.

The computer software routines were developed at Lawrence Radiation Laboratory[14]. Figure 3a is a mapping or representation in two-dimensions of the spatial interrelationships amongst the elements for March 1, 1972 as a function of all the measurements (15 dimensions) taken that day throughout the city. Such a visual display is helpful, but the information presented is incomplete and may be distorted. While it is true that the quantitative techniques of cluster analysis may not generate unique results, repeated analyses of the data for each of the 6 days listed in Table I showed the following consistent features: (1) Sb, Hg and Cu are each unique in the spatial variation of their concentrations. The Cu values are suspect because of the possibility of sample contamination from the hi-vol motors[15]. The distinguishability of Sb and Hg was observed by Belot in Paris[6]. (2) Fe, Cr and Co are generally grouped together. This is quite reasonable in a location such as Cleveland, where there are large iron and steel works. Belot in Paris found this same grouping but with Sc as a 4th constituent. (3) Sc, Al, Si, Ti, V, La, Sm, Eu, Dy, Th, Pb and Br are always found grouped together. In addition these elements have relatively little variation from site to site in their concentrations relative to TSP. This latter feature was noted by Dams et al. in their study of Gary[1]. (4) Pb and Br, while not separable quantitatively by numerical clustering techniques from the other 10 elements listed above, are seen by visual inspection to always be a bit apart from the others and relatively close to each other as is the case in Figure 3a.

Enrichment Relative to Crustal Distributions. An instructive complement to the clustering approach has been applied by a number of other workers[8] and consists of looking at the relative enrichments of the elements as compared with their relative abundances in the local rock and soil. For this purpose we chose to use the table of abundances of Mason[16] and normalize by setting Si ≡ 1. Table III contains the average enrichment factors for March 1, 1972. We note that the 3 singular elements cited above (Cu, Mg, Sb) are all significantly enriched. This is consistent with their being related to strong localized sources. The set Fe-Cr-Co indicates some possible enrichment. The uncertainty of the data makes this finding non-significant by itself, but is consistent with our earlier speculation associating them with large industrial sources which would tend to be sources of Si as well. Within the large grouping of 12 elements discussed previously, the Pb and Br stand out very distinctively with their very large and similar enrichments. The other 10 elements are found at essentially the same relative

abundances as in the earth's crust. This could well indicate the superposition of a natural background and the emissions from numerous coal burning sources in addition to relatively well distributed traffic.

Site Distinctiveness. Figure 3b is the same type of mapping as in Figure 3a, but is directed to grouping sites based on the concentrations of 34 elements at each site. While the mapping does seem to group sites, as, for example, all the U's (site 21) are together, this separation was not borne out when a quantitative cluster algorithm was applied. It is possible that the sites may not be distinguishable on the basis of this limited set of data or else the clustering algorithm may not be appropriate.

Transport by Wind

With our large data base it is possible to simultaneously look at both space and time distributions. If we assume that the major variation from one sampling day to another is meteorology induced, we can plot all the data for a single element (over 750 values) on a single map as a function of the wind. Figure 4 shows 16 log-polar plots for scandium. Each plot is centered at the site at which the data was generated. Each radial line is proportional to the average concentration observed when the vector resultant wind was inward along the radial line. The data for sites along the lake front were sorted on the basis of wind information from a lakefront airport while the rest of the data was sorted using Hopkins Airport wind data. The main drawback in attempting emission source identification by triangulation with this data set is the 24-hour sampling time, which is long relative to the duration of the wind's directional stability. We have recently developed new sampling instrumentation to overcome this problem[17] but have not yet had the time to use this new equipment to do large-scale monitoring. It is still possible, however, to draw some inferences from the spatial distribution of an element with even as little personality as scandium. For example, at the most westernly site the concentrations are relatively low and fairly uniform with respect to wind, but still perceptibly larger when the wind is from the easternly direction. This pattern is more pronounced as we look at sites closer to the region of heavy industry along the river. Thus this soil-derived element is also present in industrial emissions.

Conclusions

We have indicated an approach to analysis of a large elemental concentration data set taken at numerous sites over an extended period of time. Examples presented have emphasized the use of multiple approaches including pairwise correlation statistics, selected plotting of the data, cluster analysis, comparative enrichment studies and the use of wind transport information. Despite the large variability within the data and the considerable accuracy and precision errors it is still possible to extract useful information. We have shown that Br and Pb, as a pair, have fairly uniform distributions, are significantly enriched in TSP relative to Si when compared with their earth crustal abundances and can be used to distinguish between sites. The rare earths generally exhibit the same distributional pattern as Si, Al, and V and do not show any particular enrichment. Fe, Cr and Co show some slight indication of enrichment and have their own distributional pattern. Cu, Mg and Sb are each unique in their distributional patterns. We have also shown how a pollution-rose can be used to visualize a large body of data.

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Table I. Meteorology for the 6 days

	3/1/72	5/15/72	5/18/72	5/21/72	5/24/72	6/8/72
Average temperature (°F)	60	59	61	64	65	66
Visibility	fog,haze	haze	fog,haze	fog,haze	fog,haze	clear
Precipitation (in.)	0.20	0.66	0	0	0	0
Ave. pressure (in.)[a]	28.84	28.88	29.18	29.06	29.09	29.07
Resultant direc. (N = 0°)	190°	200°	0°	0°	20°	230°
Resultant speed (mph)[b]	15.3	6.7	3.8	3.1	4.8	10.2
Average speed (mph)[b]	15.5	9.1	5.6	6.3	7.5	10.5
Missing sample (Site #)	10	1	--	--	14	4

[a] Station elevation ~ 805 feet mean sea level
[b] Resultant speed = vectorial averaged amplitude; average speed = scalar average

Table II. Pairwise correlation coefficients

	Cleve 3/1	Cleve 5/21	Gary (ref 1)	S.F. (ref 4)	Ivory (ref 5)	Paris (ref 6)	Cleve Site 1	Cleve Site 12	Cleve Site 20
Co-Sc	.20	.08	.96	.98	.25	.92	.59	.07	.95
Sc-Th	.89	.86	.92	.97	.91	.45	.89	.77	.99
Zn-Sb	-.03	-.09	.91	-	-	.30	.54	.02	.21
Cs-Rb	.98	-.52	-	-	-	-	.83	.87	.99
Br-Pb	.60	.87	-	-	-	-	.81	.67	.76

Table III. Enrichment factors relative to earth crustal abundances normalized to Si

Na	1	V	2	Zn	200	Cd	400	Eu	2	Hg	200
Al	1	Cr	6	As	200	Sn	200	Tb	0.2	Pb	2000
Si	≡ 1	Mn	4	Se	4000	Sb	15000	Dy	2	Bi	200
Cl	500	Fe	2	Br	2000	Cs	7	Yb	5	Th	2
Sc	1	Co	4	Rb	2	La	1	Lu	6		
Ti	2	Cu	100	Ag	500	Sm	1	Hf	3		

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We wish to acknowledge the assistance of Mr. Charles Bender of Lawrence Radiation Laboratory in making RECOG available and to thank Professor Bruce Kowalski of Washington University for his insights into the application of RECOG to our problem. The LeRC version of RECOG is maintained by Mr. Glenn Cowgill. Figure 4 was computer drawn with the graphics expertise of Ms. Eileen Gorrell.

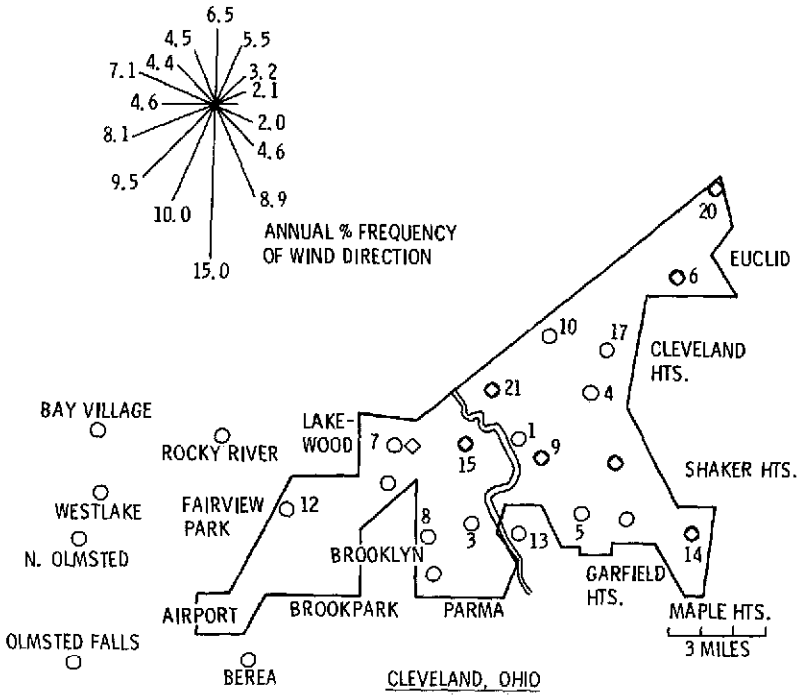
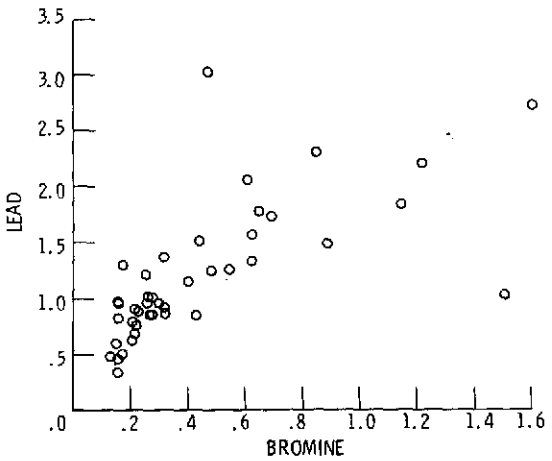
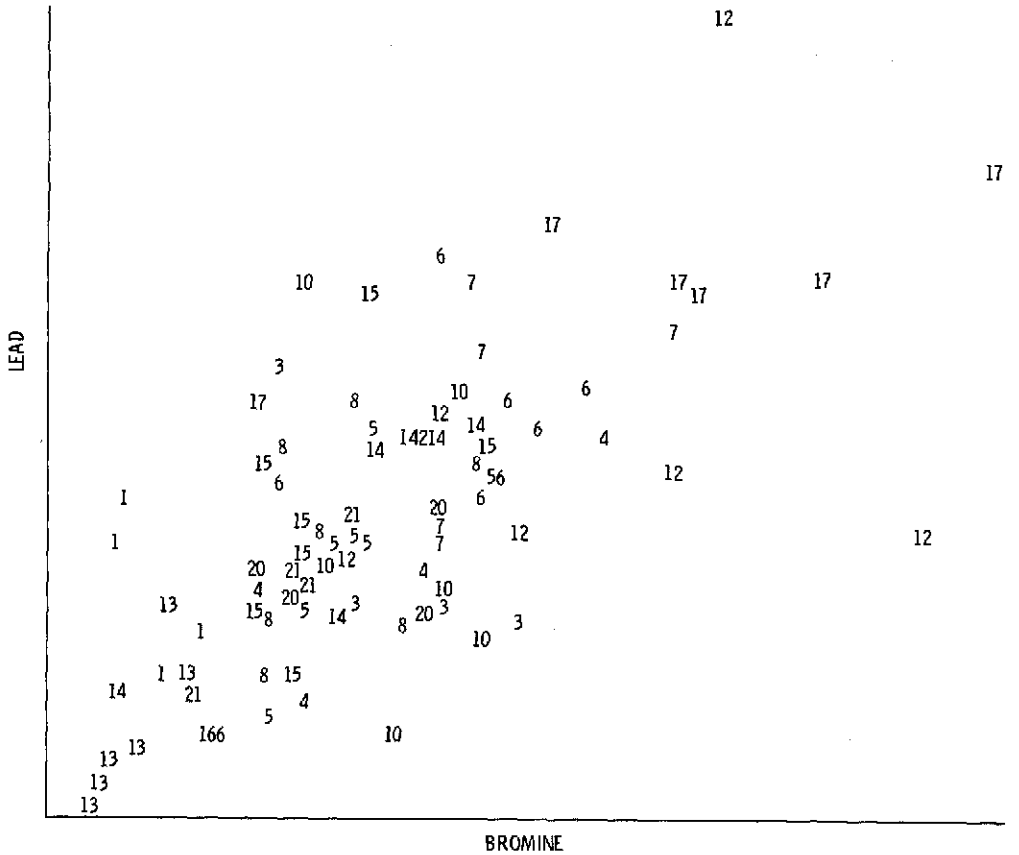


Figure 1. - Air monitoring network. The Cuyahoga River (industrial valley) is in the center, flowing north (from bottom to top) into Lake Erie. The circles, indicate air quality monitoring sites. Trace element analyses were performed at the 16 numbered sites.

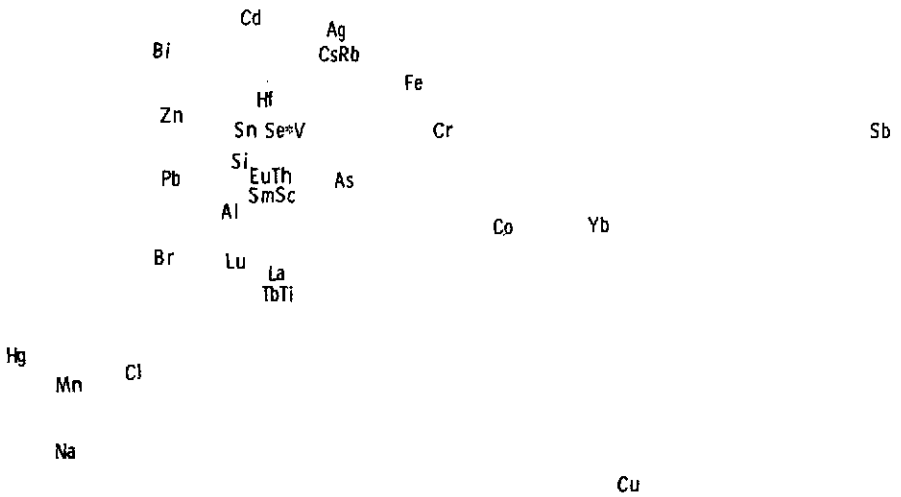


(a) Data from site no. 17 for the entire year. The mean Br/Pb = 0.314 and the correlation coefficient = 0.454.

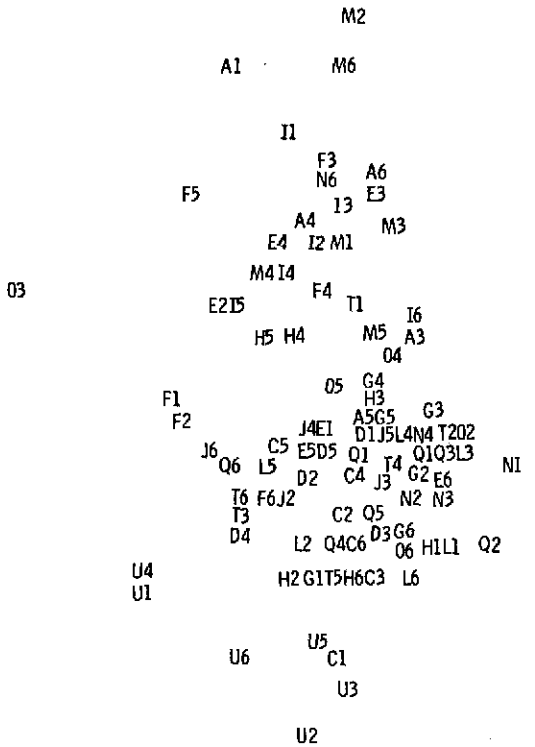


(b) Data from all 16 sites for the 6 days listed in Table I. Each datum is represented by a number (corresponding to the site numbers of Fig. 1) which identifies where it was generated.

Figure 2. - Bromine vs. lead.



(a) The elemental interrelationships are represented in 2-space as a function of the spatial distribution of their concentrations on 3/1/72 (1st day listed in Table I).



(b) The interrelationships of all the air quality samples for the 6 days listed in Table I as a function of their elemental distributions. The sites are coded by alphabetical sequention (i. e., A = 1, B = 2...U = 21) and the days by numerical correspondence to their listings in Table I (i. e., C2 = site no. 3 on 5/15/72).

Figure 3. - Representation of the data by Non-Linear-Mapping.

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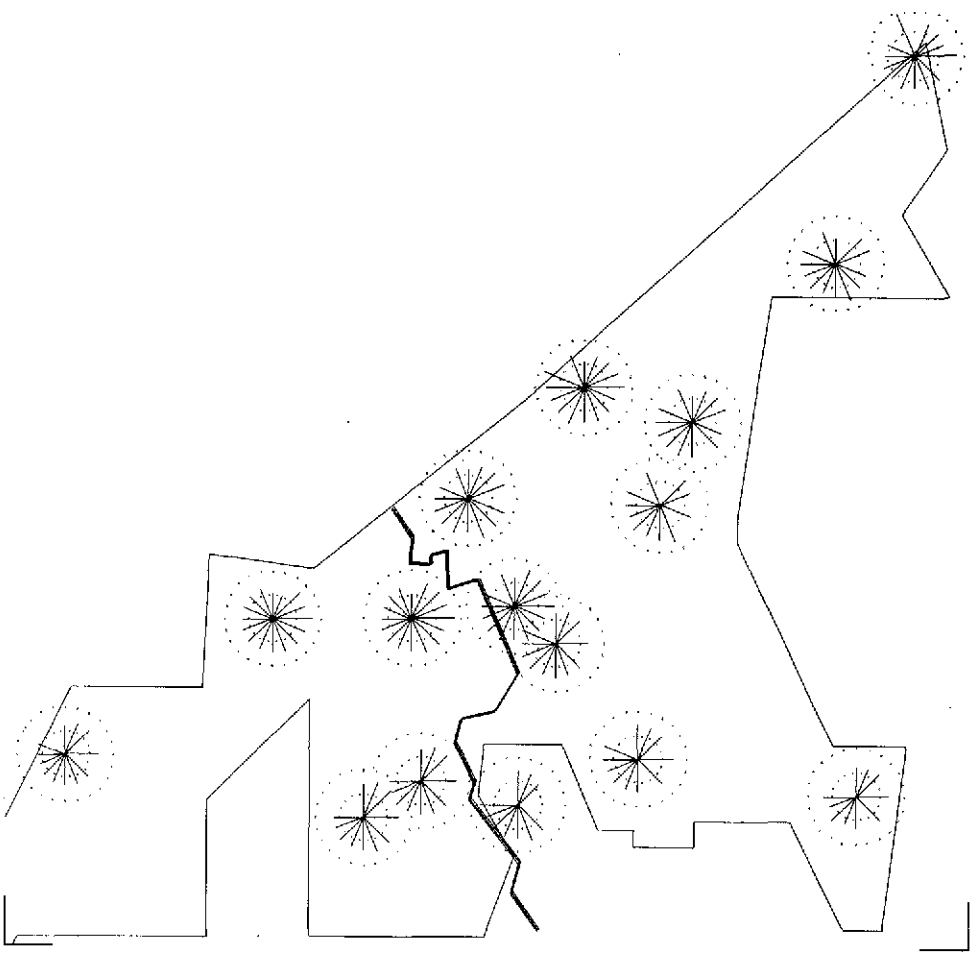

Figure 4. - Pollution - Roses for Scandium. The entire data set is used to display the 16 mean concentrations at each site as a function of the resultant (vector average) wind direction averaged over the sampling period. The graphs are polar-logarithmic with the outer scale = 10 ng/m^3 and the inner scale = 0.10 ng/m^3. The wind direction is toward the center.